

Table VI.—Solubility of Calcium Sulphate in Water in presence of various proportions of Calcium Chloride. Temperature 20°.

| Parts of $\text{CaCl}_2$ in<br>100 water. | Parts of $\text{CaSO}_4$ in<br>100 water. |
|---|---|
| 0 ·00 .....                               | ·225                                      |
| 11 ·50 .....                              | ·078                                      |
| 14 ·39 .....                              | ·063                                      |
| 19 ·80 .....                              | ·041                                      |
| 51 ·00 .....                              | ·000                                      |
| 67 ·05 .....                              | ·000                                      |

The addition of common salt, therefore, increases the solubility of calcium sulphate until the proportion of salt to water is 20 or 25 to 100. A larger quantity diminishes the solubility. Calcium chloride added to solution of calcium sulphate causes steady decrease of solubility, till when the proportion amounts to about 50 to 100 water the sulphate is practically insoluble. These results are very plainly observable in the accompanying curve (Fig. 3).

### III. "Contributions to the Chemistry of Chlorophyll. Part I."

By EDWARD SCHUNCK, F.R.S. Received April 30, 1885.

(Abstract.)

The paper treats of the products formed by the action of acids on chlorophyll. All who have worked with chlorophyll are familiar with the peculiar effects produced in solutions of chlorophyll by the action of acids. The colour is changed, and an absorption spectrum makes its appearance which differs from that of chlorophyll. According to some, these changes are due to a simple modification of the chlorophyll, others consider they are caused by the formation of products of decomposition. The latter view seems the more probable.

On passing a current of hydrochloric acid gas into an alcoholic solution of chlorophyll, a dark green, almost black, precipitate is formed at once. The greenish-yellow liquid contains substances extracted along with chlorophyll by the alcohol, and not connected with the latter. The precipitate consists essentially of two colouring matters, phyllocyanin and phylloxanthin, bodies that had been previously observed and so named by Fremy, who however did not obtain them in a state of purity. They are best separated by Fremy's method, which consists in dissolving the mixture in ether and then adding concentrated hydrochloric acid, when the liquid separates into two layers, a lower blue one containing phyllocyanin, and an upper yellowish-green one containing phylloxanthin. It is immaterial what

kind of leaves are taken for extraction, the products are always the same.

The paper deals only with the properties of phyllocyanin, which are very peculiar. After being purified in the manner described, it is obtained as a dark blue mass resembling indigo, and consisting of microscopic crystals which are generally opaque, but sometimes when very thin are translucent, and then appear olive-coloured. It stands heating to 160° without decomposition, but between that temperature and 180° it is decomposed without previously fusing, leaving a charred mass which on further heating burns away without residue. It contains nitrogen, but is free from sulphur.

Phyllocyanin is insoluble in water, petroleum ether, and ligroin, but dissolves in alcohol, ether, chloroform, glacial acetic acid, benzol, aniline, and carbon disulphide. The best solvent is chloroform. A minute quantity of the substance imparts an intense colour to any one of these solvents. It is only on diluting largely that the solutions lose their opacity. They then appear of a dull green or olive colour, and show the well-known and often described spectrum of so-called "acid chlorophyll," consisting of five bands, three of which are very dark, one of moderate intensity, and the fifth very faint.

By oxidising agents, such as nitric or chromic acid, phyllocyanin is easily decomposed, yielding yellow amorphous products, the solutions of which show no absorption bands. It shows a remarkable degree of permanence as compared with chlorophyll, when exposed to the combined action of air and light. A chloroformic solution contained in a loosely stoppered bottle may be exposed for weeks or even months to alternate sunlight and diffused daylight before its peculiar colour and all trace of absorption bands have disappeared. When the process is complete a yellow liquid results, which contains several products, all of them amorphous, one being easily soluble in water and exceedingly bitter to the taste. The decoloration of a chlorophyll solution under the same circumstances would take place in a day or two.

A small quantity of bromine added to a chloroformic solution of phyllocyanin changes the colour to a bright grass-green, which exactly resembles that of a chlorophyll solution. By a further addition of bromine, the solution loses its green colour and acquires a reddish hue; it now shows the same spectrum as a phyllocyanin solution; but the bands are all shifted towards the red end. An excess of bromine produces no further change. On passing chlorine gas through the solution in chloroform, it passes through the same phases of colour, first becoming grass-green, then reddish, but a further change takes place on continuing to pass chlorine through the solution, which now becomes yellow, finally pale yellow, all traces of absorption bands at the same time disappearing. The products both with bromine and chlorine are amorphous.

Phyllocyanin dissolves easily in concentrated sulphuric, hydrochloric, and hydrobromic acids, yielding dark blue solutions, which show spectra differing from that of phyllocyanin, and no doubt contain compounds of the latter with acids. These compounds however are unstable, for on the addition of water to the solutions, phyllocyanin is precipitated unchanged. Phyllocyanin shows no tendency to combine with weaker acids, such as phosphoric, oxalic, tartaric, or citric acid.

Phyllocyanin dissolves easily in dilute caustic potash or soda lye. The solution gives precipitates of various shades of green with earthy and metallic salts, such as barium chloride, calcium chloride, lead acetate, and cupric acetate, and these might be called phyllocyanates. It seems however that by mere solution in alkali, phyllocyanin undergoes some change, for if acetic acid in excess be added to the solution and it be then shaken up with ether, the precipitate dissolves in the ether, giving a solution which shows the bands of phyllocyanin, but if the whole be left to stand some time, the colour of the ethereal solution changes from green to brown, and it now shows a distinct and peculiar spectrum, characterised by two bands in the red and two fine but well-marked bands in the green, the third and fourth bands of phyllocyanin having disappeared, while the fifth still remains. The body yielding this spectrum has been prepared and found to yield microscopic crystals like phyllocyanin. A different product is formed when hot alkaline lye, or, what is better, boiling alcoholic potash or soda is employed. It crystallises in small rosettes, which are green by transmitted, of a fine purple by reflected light. Its solutions have a dull purple colour, and exhibit a distinct spectrum characterised by a broad very dark band in the green. It may be identical with one of the products obtained by Hoppe-Seyler from his chlorophyllan with alkalis.

The action of aniline on phyllocyanin is peculiar and interesting. When the two are heated together in a sealed tube to 130° the phyllocyanin disappears entirely, giving several products, one of which is colourless and crystallises in white needles. The second, which may be an anilide, yields solutions which are quite red, and show a characteristic spectrum having three fine but distinct bands in the red, and three other very strong bands, one in the yellow, one in the green, and one at the edge of the blue. No similar compound is formed when ammonia is used in place of aniline.

The concluding part of the paper treats of what may be called double compounds of phyllocyanin, into which metals and acids, especially organic acids, enter as constituents. Phyllocyanin seems to act the part of a weak base, uniting with strong acids and forming unstable compounds. In acetic acid it merely dissolves without yielding any compound. In like manner, when freshly precipitated

cupric oxide or zinc oxide is added to a solution of phyllocyanin in boiling alcohol no combination takes place. A very different effect is observed when either of the two oxides is employed along with acetic acid. When cupric oxide is added to a solution of phyllocyanin in boiling acetic acid the solution acquires at once a deep greenish-blue colour, and it no longer contains uncombined phyllocyanin, for its spectrum is different, and on standing it deposits lustrous crystals, which doubtless consist of a compound containing phyllocyanin, acetic acid, and copper. If zinc oxide be employed a similar effect is observed, the liquid acquires an intense green colour like that of a chlorophyll solution, and now contains the corresponding acetate of phyllocyanin and zinc. The same phenomenon is seen when ferrous oxide, manganese oxide, or silver oxide is taken, liquids of various shades of green being obtained which contain phyllocyanin compounds, but no similar compounds are formed when potassium, sodium, barium, calcium, magnesium, or lead acetate is employed. Acetic acid is, however, not the only acid which yields the reaction. If palmitic, stearic, oleic, tartaric, citric, malic, or phosphoric acid be employed, it takes place just as with acetic acid, but in some cases time is required for its completion. Oxalic acid, however, seems to be without effect, and tartaric acid fails in some cases.

The various compounds have a number of properties in common, though the several classes differ, *inter se*, in some important particulars. They all dissolve more or less readily in alcohol, ether, chloroform, benzol, and carbon disulphide, but are all insoluble in water with the exception of the phyllocyanin manganese acetate, which dissolves readily therein. The solutions have a green colour varying from grass-green, like that of chlorophyll solutions, to a fine bluish-green or blue, and they show peculiar spectra. The alcoholic solutions remain unchanged when sulphuretted hydrogen is passed through them, no precipitate is formed, and the solutions on evaporation leave the various compounds with their original properties. It is only on incineration that the presence of metallic constituents is detected. Lastly, they are all soluble in dilute alkaline lyes, and are reprecipitated unchanged on the addition of acetic acid. These reactions make it somewhat doubtful whether these compounds are to be considered as double salts in the ordinary acceptation, and whether the metallic constituents may not rather be contained in them somewhat in the same way as the iron in hematin. Of the various compounds those belonging to the cupric class are the most stable; they are not decomposed by boiling hydrochloric acid. The zinc compounds, on the other hand, are very readily decomposed by hydrochloric acid, yielding phyllocyanin.

The behaviour of phyllocyanin towards zinc oxide in the presence of acids may serve to explain a peculiar phenomenon first observed by

Professor Church, and subsequently described by Tschirch. The former took chlorophyll that had become brown on standing, and acting on it with zinc powder obtained a body yielding green solutions, which he took to be regenerated chlorophyll. Tschirch acted on Hoppe-Seyler's chlorophyllan with zinc powder and observed the same phenomena, the conclusion at which he arrived being the same, viz., that chlorophyll is reproduced from chlorophyllan by reduction. It is probable, however, that what they obtained was in reality a zinc compound of phyllocyanin, and would have been formed just as well by using zinc oxide. Chlorophyllan is probably an impure substance containing some fatty acid along with phyllocyanin, so that by the action of zinc oxide it may yield a compound similar to those above mentioned. The experiment was tried with the crude product obtained by passing hydrochloric acid gas into a solution of chlorophyll. Some of this was dissolved in alcohol, and the solution was boiled with zinc oxide, when it gradually became of a bright green like a solution of chlorophyll, but its spectrum differed, being identical with that of the zinc compounds obtained directly from phyllocyanin.

IV. "On the Electric Resistance of a New Alloy named Platinoid." By J. T. BOTTOMLEY, M.A., F.R.S.E. Communicated by Sir W. THOMSON. Received May 5, 1885. Read May 7, 1885.

In the course of a series of experiments on the electric resistance of various metals and alloys, and in particular on the variation of the electric resistance of these metals and alloys with temperature, I have examined a new alloy (called by the inventor platinoid), which has turned out to have important properties.

This alloy is the invention of Mr. F. W. Martino, of Sheffield; and I have to acknowledge my indebtedness to Mr. Martino for having provided me with specimens of his new alloy and given me information regarding it; and for having supplied me with wires specially drawn down to the finer gauges for my experiments.

The inventor, searching experimentally for a means of rendering tarnishable metals and alloys less tarnishable, had satisfied himself that the addition of pure metallic tungsten imparted greater density to alloys, and likewise less tendency to oxidation. Having found a mode of combining a small quantity of tungsten with copper, nickel, and zinc, he produced a white alloy resembling the alloys of silver, which proved very little tarnishable under atmospheric